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MECHANISM OF REGENERATION OF BROKEN CHEMICAL BONDS IN THE SPATIAL STRUCTURE OF GLASSES AND NATURAL HIGH-SILICA MATERIALS

M. S. Movsisyan[1]

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It is shown that it is possible to restore partially the chemical bonds and spatial structure of high-silica natural rocks and glass broken by crushing and milling. The obtained materials (blocks, plates, lightweight articles, etc.) can be used in the building industry.

In accordance with the concepts of the theory of the chemistry of silicates, natural high-silica rocks (tuffs, slags, basalts, granites, etc.), glasses, and vitreous substances are predominantly composed of silica (60 – 80%) which combines with the oxides of some metals forming a spatial skeleton of siloxane groups in the form of $\equiv Si-O-Si\equiv$ chains. In some cases the silicon atoms in these substances are substituted by the atoms of other elements ($\equiv Si-Me-O-Si\equiv$) that give specific physicochemical and other properties to the substance (rock, glass) [1]. In the treatment of such materials (cutting, crushing, milling, grinding, etc.), the spatial chain or tetrahedral structures are broken in accordance with the following scheme:

$$\equiv Si-O-Si\equiv \rightarrow \equiv Si-O- + -Si\equiv. \qquad (1)$$

As a result, free chemical bonds that cannot exist long in such a state appear on the surface of the crushed particles [2, 3]. They interact with various substances (oxides, salts, acids, alkalis) joining oxides of various metals depending on the composition of the environment (R_2O, RO, R_2O_3, etc.),

$$\equiv Si-O- + R_2O + -Si\equiv \rightarrow \equiv Si-OR + RO-Si\equiv, \qquad (2)$$

where R is used to denote H, Na, K, and other elements.

If R is represented by elements of the first group of the periodic system (H, Na, K, etc.), the compound has the form of $\equiv Si-OH$, $\equiv Si-ONa$, etc. If R is represented by an element of the second, third and higher groups, the element enters the siloxane groups joining two broken parts and forming larger chains, i.e.,

$$\equiv Si-O- + RO + -Si\equiv \rightarrow \equiv Si-O-R-O-Si\equiv. \qquad (3)$$

The formed substance can have the form

$$\begin{matrix}\equiv Si-O\diagdown & \\ & Me, \\ \equiv Si-O\diagup & \end{matrix}$$

i.e., the metal ions in the siloxane chain can be represented by an externally attached element that can later attract hydroxyl or other groups.

Thus, in the process of crushing, milling, grinding and spraying of the rock or glass, the spatial bonds break. In some cases they can be partially regenerated by connecting two shortened groups into a longer spatial chain.

It can be seen from reactions (2) and (3) that in order to regenerate two broken groups, R_2O should be removed in the process of reaction (2). Then the old bonds are restored by condensation reactions (1) – (3) [2, 3]

$$\equiv Si-OR + RO-Si\equiv \rightarrow R_2O + \equiv Si-O-Si\equiv. \qquad (4)$$

If the role of R is played by hydrogen, a water molecule is liberated with the formation of a two times larger silicate particle. If R is represented by a bi-, trivalent or higher valence metal, the reaction occurs in accordance with scheme (3) or more complexly with branching, i.e., the process has the form of polymerization with the formation of chain or polyhedral spatial structures.

This can be represented as follows. In crushing, milling or cutting of the rock, free chemical bonds appear on the surface of the particles and attach either hydroxyl groups or elements from the environment with the formation of $\equiv Si-OH$, $\equiv Si-OR$ and other groups on the surface of the particles. The general pattern of the process looks like

$$\begin{matrix} & OH(R) \\ O\diagup & \end{matrix}$$

[1] Institute of General and Inorganic Chemistry of the National Academy of Sciences of the Republic of Armenia, Erevan, Armenia.

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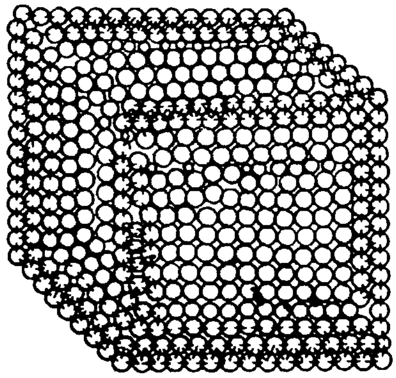

Fig. 1. Diagram of regeneration of broken bonds in crushed rock or glass in the form of a polyhedral structure.

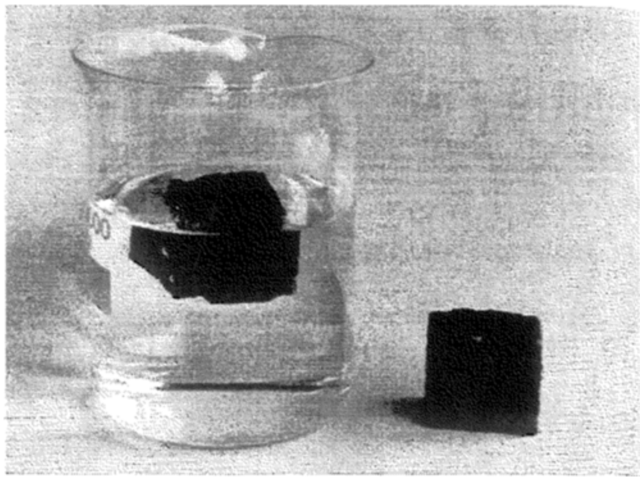

Fig. 2. Lightweight heat-insulating material obtained from tuff.

When two such particles (grains) move close to each other, they can split out water in accordance with the reaction

$$\mathrm{O}\overset{/\mathrm{OH}}{} + \mathrm{O}\overset{/\mathrm{HO}}{} \rightarrow \mathrm{O}\overset{/\mathrm{O}\backslash}{}\mathrm{O} + H_2O \qquad (5)$$

with the formation of an oxygen-bridge bond.

If the environment contains bi-, trivalent, and higher valence metals instead of univalent ones, the reaction can be represented as

$$\mathrm{O}\overset{/\mathrm{OH}}{} + \mathrm{Me} + \mathrm{O}\overset{/\mathrm{HO}}{} \rightarrow$$
$$\rightarrow \mathrm{O}\overset{/\mathrm{O-M-O}\backslash}{}\mathrm{O} + H_2O, \qquad (6)$$

i.e., we have polymerization. Thus, the particles move close to each other, forming the described spatial structure (Fig. 1). The particles attached through cross bridges form strongly bonded spatial structures that can resist external forces.

All this indicates that with crushing and milling of natural volcanic stones and rocks as well as silicate materials (glass, ceramics, etc.), the bonds of their spatial structure can be broken and regenerated in the material with restoring the physicochemical and mechanical properties of the original rocks and even exceeding them in some cases.

Let us consider, for example, the possibility of using waste natural stones formed in mining, which are pushed aside and occupy considerable fertile territories [4]. After regenerating the broken bonds, they can be used for the production of facing or partition plates, bricks, blocks, panels and other building materials even without using cement.

The substances that promote the regeneration of broken bonds will be called regenerators. Among other substances, this can be water (see reaction (2)). Three conditions should be met for the restoration of broken bonds, namely,

(1) The regenerator should be a liquid. This means that when it is used, each particle is enclosed by a thin molecular layer of the liquid where the regeneration processes occur more easily. The liquid medium intensifies the mobility of the particles and their compaction.

(2) The particles should contact each other. The closer the packing of the particles of the disintegrated rock, the greater the number and area of the contacting surfaces, and hence the regenerated bonds. The higher the degree of disintegration and the smaller the size of the particles, the higher the specific surface area of the powder, the greater the number of contacting surfaces and regenerated bonds. The greater the number of regenerated bonds, the stronger the fabricated article. In order to increase the density, the mixture should be pressed.

(3) Mixing of finely milled powder with the regenerating liquid gives a quite unstable mobile mixture that can easily deteriorate; the bonds appearing in it can easily break in the given medium. The regenerated bonds should be fixed so that the product could resist external actions, i.e., acquire strength and other properties.

The regeneration of previously broken bonds can be controlled so that the product will acquire a density substantially different from that of a monolithic material. For example, it is known that the density of glass fluctuates within 2.5 – 2.6 g/cm^3 and the density of tuff (both in different deposits and in the same mine depending on the depth of the layer) fluctuates within 1.2 – 1.8 g/cm^3. It is possible to fabricate lightweight floating materials with a bulk density of 0.5 – 0.8 g/cm^3 (Fig. 2) from such heavy and dense materials as glass, granite, basalt, or tuff.

We used in our experimental study a certain amount of regenerating liquid and powdered natural slag from the Ashtarakskoe deposit (Armenia) in the following proportion: 75 – 93% powder, 7 – 25% regenerating liquid. The mixture was carefully stirred, poured into metallic molds, and pressed at 0.5 – 2.5 MPa. The obtained cylindrical briquettes (1.8 cm in diameter and 2.3 – 3.5 cm high) were dried in air, then in a desiccator at 100°C for 60 min, after which they were heat treated at 500°C for 40 min. After total removal of moisture, the specimens were tested for compressive strength

with determination of their strength parameters. The results are presented in Tables 1 and 2.

It is known that with an increase in the amount of the regenerating liquid, the strength parameters are increased. The optimum amount is equal to 15 – 20% above which the liquid phase flows out of the mixture in the shaping process, decreasing the strength (see condition (1)). With an increase in the pressing pressure, the density and strength parameters of the specimens increase too (see condition (2)).

In pressing the moistened mixture, the specimens break easily even due to slight shaking. After drying and heat treatment, they withstand considerable forces (see condition (3)). As the composition of the regenerating liquid is changed from water to magnesium, calcium, or aluminum salts, the resistance to fracture increases.

It follows from the data in Table 2 that when water is used as the regenerating liquid in the amount of 10%, the compressive strength increases with an increase in the pressing pressure. In pressing at 0.5 MPa, the strength of the specimens amounts to 0.8 MPa, whereas at 2.5 MPa it attains 1.6 MPa.

In addition, when the regenerating liquid is a liquid containing magnesium, calcium or aluminum cations, the strength parameters increase markedly (see Table 1). For example, with the use of solutions that contain magnesium ions with a concentration of MgO equal to 70 g/liter, the strength parameters are almost the same as with the use of water, whereas with the use of calcium-bearing solutions of the same concentration, the resistance to the load increases by a factor of 5 – 6 relative to the aqueous solution and attains 1.6 MPa instead of 0.24 – 0.32 MPa.

TABLE 1

Shaping pressure, MPa	H_2O + slag		$Ca(NO_3)_2$ + slag		$Mg(NO_3)_2$ + slag		Al_2O_3 + slag	
	bulk density, g/cm^3	compressive strength, MPa	bulk density, g/cm^3	compressive strength, MPa	bulk density, g/cm^3	compressive strength, MPa	bulk density, g/cm^3	compressive strength, MPa
Regenerating liquid/powder ratio (%), 7/93								
0.5	–	–	–	–	–	–	1.40	0.290
1.0	–	–	1.54	0.076	1.70	0.060	1.50	1.260
1.5	–	–	1.41	0.157	1.65	0.104	1.60	2.000
2.0	–	–	1.64	0.400	1.63	0.108	1.60	3.208
2.5	–	–	1.61	0.404	1.75	0.156	1.70	3.900
Regenerating liquid/powder ratio (%), 10/90								
0.5	1.43	0.040	1.76	0.501	1.65	0.040	1.41	1.040
1.0	1.53	0.140	1.69	0.750	1.70	0.076	1.53	4.000
1.5	1.75	0.140	1.71	0.800	1.80	0.128	1.59	7.600
2.0	1.42	0.140	1.79	0.650	1.81	0.190	1.65	8.600
2.5	1.59	0.240	1.80	0.470	1.90	0.195	1.69	8.800
Regenerating liquid/powder ratio (%), 15/85								
0.5	1.48	0.140	1.39	0.480	1.33	0.040	1.56	6.000
1.0	1.64	0.140	1.49	0.570	1.60	0.084	1.57	8.800
1.5	1.63	0.160	1.58	0.630	1.81	0.177	1.64	14.840
2.0	1.64	0.200	1.58	0.750	1.81	0.177	1.64	14.840
2.5	1.86	0.240	1.61	1.100	1.59	0.200	1.79	21.200
Regenerating liquid/powder ratio (%), 20/80								
0.5	1.45	0.140	1.37	1.370	1.66	0.124	1.47	10.400
1.0	1.55	0.140	1.46	1.520	1.70	0.184	1.57	17.400
1.5	1.53	0.160	1.55	1.770	1.80	0.180	1.63	22.800
2.0	1.66	0.160	1.63	1.725	1.83	0.328	1.77	17.400
2.5	1.61	0.240	1.67	1.520	1.94	0.325	1.75	17.400
Regenerating liquid/powder ratio (%), 25/75								
0.5	1.41	0.140	–	–	1.44	0.204	1.53	10.000
1.0	1.54	0.160	–	–	1.47	0.204	1.64	13.600
1.5	1.67	0.160	–	–	1.57	0.180	1.64	18.800
2.0	1.74	0.240	–	–	1.83	0.240	1.65	18.800
2.5	1.75	0.320	–	–	1.78	0.180	1.76	13.600

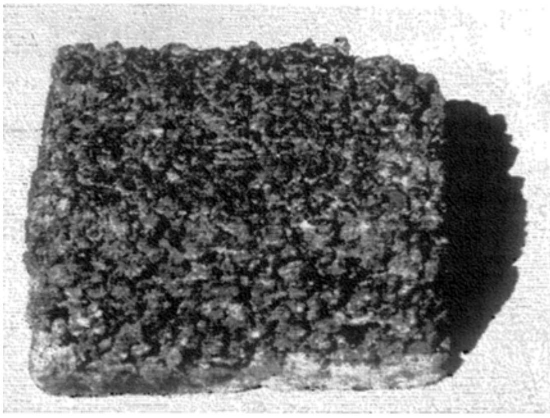

Fig. 3. Regenerated bonds in the fabricated building material (bound individual particles of crushed rock can be observed).

With the use of solutions containing aluminum with a concentration of Al_2O_3 equal to 70 g/liter, the compressive strength attains 20 – 25 MPa. This means that when H^+ ions are replaced by Mg^{2+}, Ca^{2+}, Al^{3+}, the material undergoes polymerization reactions (6), i.e., the particles move close to each other forming a spatial polyhedral structure (see Fig. 1) and their metal-oxide bridges create strong bonds that can resist breaking forces acting from the outside.

Our experiments showed that the regenerating medium is of a great importance. It should be a liquid. When the liquid is mixed with milled rock or glass powder, the particles of these materials are wet by a thin molecular layer of the liquid, causing a reaction of type (2). For the reaction between the broken particles to continue, they should contact each other. Compaction and the liquid medium create the appropriate conditions. The latter turns the mixture into a mobile mass and even inconsiderable compaction (0.5 – 2.5 MPa) moves the particles close to each other (Fig. 3), and the bonds recover in accordance with (1) – (6).

A solution of a substance that possesses bonds affine to those of the regenerated material will be the best regenerating liquid. Such regenerators can give a developed skeleton of spatial chains possessing a high strength.

We tested an alkaline silicate solution as a regenerating liquid for milled glass powder or natural volcanic rocks (tuffs, slags).

It was established that when the amount of the regenerating liquid is increased, the strength parameters increase. For example, at a 5% concentration of the liquid in the mixture and a treatment temperature of 100°C, the strength of the specimen was 6.12 MPa, whereas the use of a regenerating liquid with a 10% concentration under the same conditions provided a strength of 29.76 MPa, and the use of a 20% concentration of the liquid provided 79.77 MPa. With an increase in the temperature to 150°C and using the same concentrations of the regenerating liquid, we obtained specimens with a strength diminished to 5.21, 16.97, and 27.20 MPa respectively. With an increase in the treatment temperature above 200°C, the strength of the specimens virtually did not change, and in the 300 – 400°C range it remained virtually constant. This is explainable by the fact that in preparation of the mixture, it undergoes hydration (like the processes that occur in cement) [3] with the formation of hydrosilicates of predominantly amorphous nature. It is possible that at a lower temperature (100 – 150°C), the crystal hydrates do not decompose or the decomposition process occurs incompletely, which results in the formation of a powerful spatial skeleton of hydrosilicates, increasing the strength parameters of the specimens. It seems that at 200 – 400°C the crystal hydrates decompose fully and the part of the constitutional water that forms the additional strong skeleton is removed, which diminishes the strength of the specimens.

Figure 4 presents the strength parameters of a mixture of powdered natural volcanic rocks (tuffs, slags) with glass powder in the ratio of 80 to 20% with addition of a regenerating liquid, i.e., an alkaline silicate solution.

TABLE 2

Shaping pressure, MPa	H_2O + glass powder		$Ca(NO_3)_2$ + glass powder	
	bulk density, g/cm^3	compressive strength, MPa	bulk density, g/cm^3	compressive strength, MPa
	Regenerating liquid/powder ratio (%), 7/93			
0.5	–	–	1.04	0.200
1.0	–	–	1.08	0.640
1.5	–	–	1.04	0.800
2.0	–	–	1.13	1.600
2.5	–	–	1.15	1.600
	Regenerating liquid/powder ratio (%), 10/90			
0.5	–	–	1.05	0.800
1.0	–	–	1.07	1.060
1.5	–	–	1.08	1.101
2.0	–	–	1.12	2.030
2.5	–	–	1.13	1.600
	Regenerating liquid/powder ratio (%), 15/85			
0.5	1.25	0.200	1.04	1.904
1.0	1.22	0.200	1.26	1.356
1.5	1.25	0.280	1.29	5.274
2.0	1.36	0.300	1.32	6.400
	Regenerating liquid/powder ratio (%), 20/80			
0.5	–	–	1.03	4.177
1.0	–	–	1.19	3.333
1.5	–	–	1.13	3.434
2.0	–	–	1.24	3.603
2.5	–	–	1.26	3.430
	Regenerating liquid/powder ratio (%), 25/75			
5.0	1.24	0.400	–	–
13.0	1.30	1.200	–	–
25.0	1.31	2.350	–	–
37.0	1.35	2.900	–	–

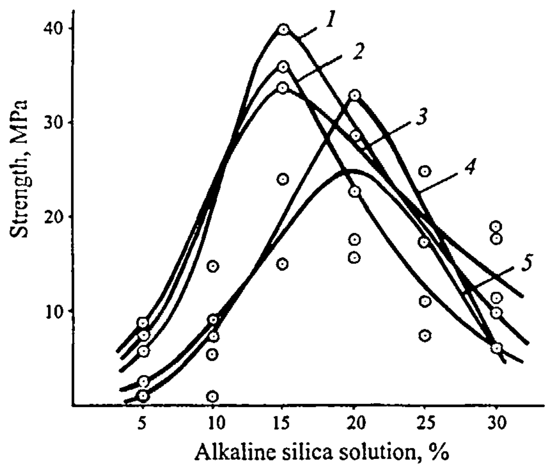

Fig. 4. Dependence of the strength of a mixture of powders of natural slag with glass powder on the amount of regenerating liquid (alkaline silica solution). The specimens were shaped at a pressure of: *1*) 0.5 MPa; *2*) 1.0 MPa; *3*) 1.5 MPa; *4*) 2.0 MPa; *5*) 2.5 MPa.

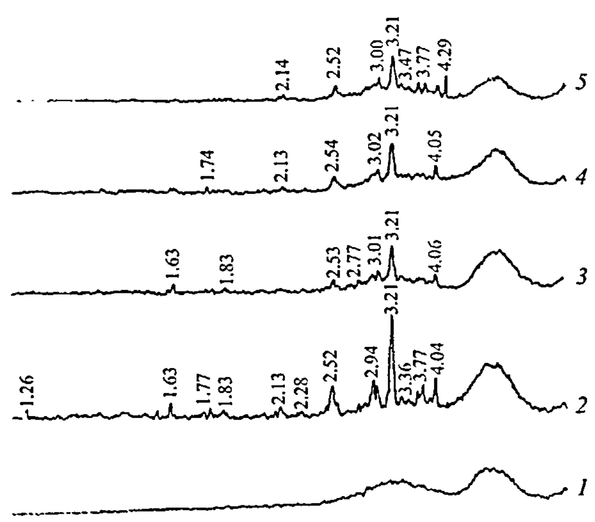

Fig. 5. Diffractograms of glass powder (*1*), natural slag (*2*), a mixture of a glass powder with a reducing liquid (*3*), a mixture treated at 500°C (*4*), and a mixture treated at 800°C (*5*).

It can be seen from the curves that 15 – 20% of the regenerating liquid in the total mass of milled powders is the optimum amount that provides the highest strength parameters (30 – 40 MPa). Parts with such strength can be used as wall blocks, partition and facing plates with a colored smooth surface, or for fabricating a lightweight porous material with a bulk density of 0.5 – 0.8 g/cm^3 and a compressive strength of 2 – 5 MPa that floats in water and can be used either as heat insulation or in the form of lightweight blocks and partition plates.

A mixture of natural slag from the Ashtarakskoe deposit and glass powder in the ratio of 80 to 20% with an additive of 15% alkaline silicate solution was subjected to x-ray analysis. The diffractograms are presented in Fig. 5; the powder was represented by a continuous amorphous mixture.

The diffractogram of the natural slag exhibits lines of interplanar distances of calcium aluminosilicates of the type of anorthite $Ca(Al_2Si_2O_3)$, although the major part of the slag is amorphous. Since the slag is represented by 11% Fe_2O_3, about 15% Al_2O_3, and the remainder is SiO_2, it can be assumed that it contains aluminum- and iron-containing silicates of a predominantly amorphous nature accompanied by crystalline silicates.

The same crystalline phase passes into the mixture of the mentioned components after heat treatment at 500 and 800°C for 30 min (see Fig. 5). However, the diffractogram exhibits a limited number of maxima and a shift of the lines present in the diffractogram of the slag. This indicates that the fabricated specimen undergoes physicochemical processes in pressing, which form the spatial skeleton of the building material with regeneration of previously broken bonds.

The behavior of the lines of the interplanar distances shows that their intensity diminishes relative to that of natural slag, the number of maxima of the crystalline phase decreases, and new lines appear somewhat different from the principal lines of the interplanar distances of the slag. This gives grounds for assuming that the finished specimen undergoes formation of new phases of a predominantly amorphous character.

Thus, the regeneration of previously broken chemical bonds in the spatial structure makes it possible to obtain colored smooth-surface building parts applicable as facing and heat-insulating materials, wall blocks, and bricks from natural or industrial waste of rocks and materials.

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